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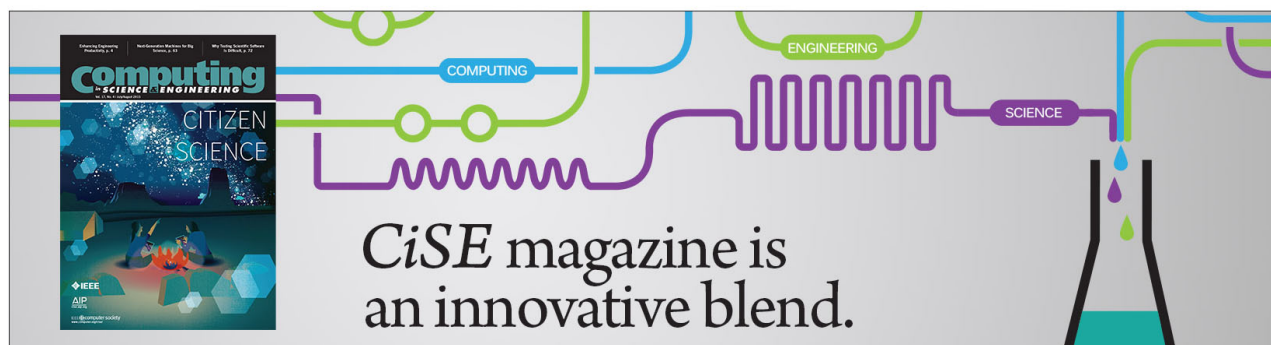
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Material degradation of liquid organic semiconductors analyzed by nuclear magnetic resonance spectroscopy

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Liquid organic light-emitting diodes (liquid OLEDs) are unique devices consisting only of liquid organic semiconductors in the active layer, and the device performances have been investigated recently. However, the device degradation, especially, the origin has been unknown. In this study, we show that material degradation occurs in liquid OLEDs, whose active layer is composed of carbazole with an ethylene glycol chain. Nuclear magnetic resonance (NMR) experiments clearly exhibit that the dimerization reaction of carbazole moiety occurs in the liquid OLEDs during driving the devices. In contrast, cleavages of the ethylene glycol chain are not detected within experimental error. The dimerization reaction is considered to be related to the device degradation. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4928515>]

I. INTRODUCTION

The external quantum efficiency (EQE) of liquid OLEDs is still low compared to OLEDs consisting only of solid-state organic semiconductors, typically less than one percentage.¹⁻⁵ However, liquid OLEDs have unique characteristics not shared by OLEDs⁶ and the EQE has increased by twenty five times over the past several years. Liquid OLEDs have simple device architectures; liquid semiconductors are sandwiched between two substrates with electrodes, which can be fabricated without using high vacuum deposition processes. Liquid OLEDs are expected to allow the realization of truly flexible displays, because both cracks of emitting layer and detachments between the liquid emitting layer and electrodes do not occur when the displays are bent. However, the fundamental characteristics are at a primitive stage and the device lifetime is very short at present.³ Thus, it is important to reveal the degradation mechanisms in liquid OLEDs. For solid-state OLEDs, the clarification of the origin of the device degradation has been attempted.⁷⁻¹³ However, the degradation mechanisms of liquid OLEDs have not been investigated yet. To reveal the degradation mechanisms of liquid OLEDs, it is important to identify the degraded molecules produced in driving liquid OLEDs, which will provide guidelines for material designs with high durability. In general, solution NMR is useful to identify the chemical structures of organic molecules. Therefore, in this study, we have investigated the material degradation in liquid OLEDs by solution NMR.

II. EXPERIMENTS

The chemical structure of materials used in the liquid OLEDs are shown in Fig. 1(a). 9-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-9H-carbazole (TEGCz) and 9,9'-{2-[2-(2-methoxyethoxy)ethoxy]}

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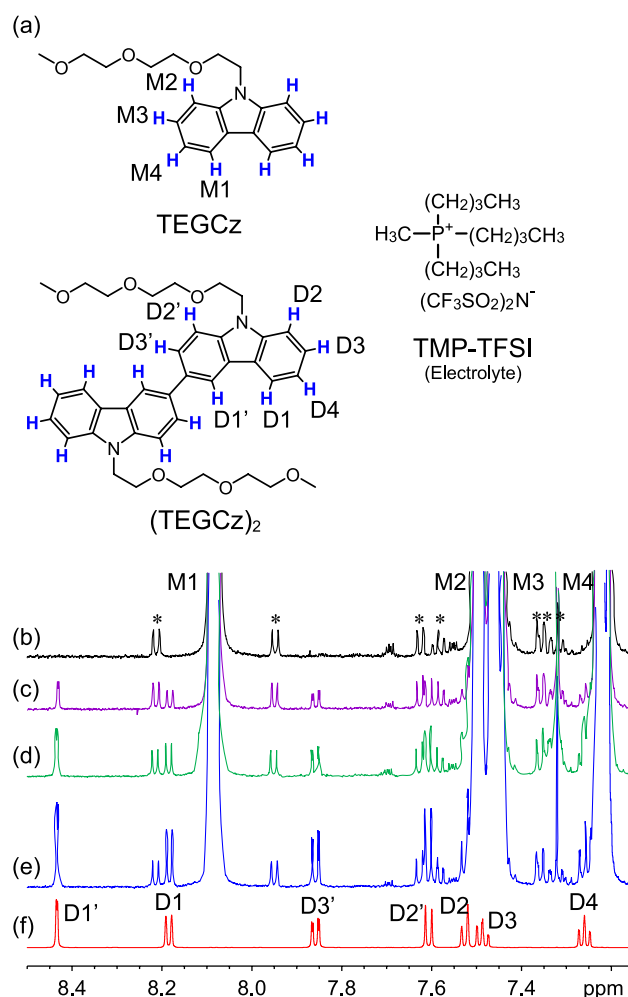


FIG. 1. (a) Chemical structures of TEGCz, (TEGCz)₂, and TMP-TFSI. Hydrogen atoms in the ethylene glycol chain are omitted for clarity. The assignments of protons are shown. ¹H NMR spectra of TEGCz with 0.25 wt% TMP-TFSI; (b) before, after driving for (c) 11 s, (d) 30 s, and (e) 50 s. ¹H NMR spectrum of (TEGCz)₂ with 0.25 wt% TMP-TFSI before driving is also shown in (f) for comparison.

ethyl}-3,3'-bis(9*H*-carbazole) [(TEGCz)₂] were used as liquid organic semiconductors and tributylmethylphosphonium bis(trifluoromethanesulfonyl)imide (TMP-TFSI) was doped into the TEGCz or (TEGCz)₂ layer as a liquid electrolyte. TEGCz and (TEGCz)₂ were synthesized according to the previous reports.^{3,14} TMP-TFSI was purchased from Tokyo Chemical Industry. The devices were composed of indium-tin-oxide (ITO)/0.25 wt% TMP-TFSI doped TEGCz (10 μm)/ITO. The devices were driven at 1 mA for 11, 30, and 50 s. Three different solution NMR experiments were performed to reveal the material degradation in liquid OLEDs. First, we carried out ¹H NMR experiments of TEGCz with 0.25 wt% TMP-TFSI after the degradation for 11, 30, 50 s. ¹H NMR experiments of TEGCz and (TEGCz)₂ with 0.25 wt% TMP-TFSI before degradation were also carried out for comparison. Second, DOSY experiment was carried out to separate different organic materials in the devices after driving for 50 s. COSY experiments were carried out for the assignments of resonance lines. All the following solution NMR experiments were performed on a Bruker AVANCE III 600 MHz US Plus spectrometer with a double resonance 1.7 mm probe using dichloromethane-*d*₂ or chloroform-*d*.

III. RESULTS AND DISCUSSIONS

Figure 1(b)–1(e) shows expanded ¹H NMR spectra of the materials in the active layer of the liquid OLEDs. The assignment of resonance lines were carried out by a ¹H-¹H correlation

spectroscopy (^1H - ^1H COSY) experiment (see Fig. S1–S4 of supplementary material).¹⁵ Figure 1(b) shows the NMR spectrum of the materials in the active layer before driving. Figure 1(c), 1(d), and 1(e) show the NMR spectra after driving for 11, 30, and 50 s, respectively. * marks in the figure represent carbon satellites for the peak of TEGCz. The resonance lines at 8.43 (D1'), 8.18 (D1), and 7.86 (D3') ppm, which were not observed in Fig. 1(b) (before driving), were clearly found in all of Fig. 1(c), 1(d), and 1(e) (after driving). Moreover, the intensity of these peaks increase with the driving times of the liquid OLEDs. Therefore, these peaks are reasonably assigned to ^1H in degraded molecules and TEGCz is assumed to be decomposed into degraded molecules in the liquid OLEDs. If the degradation occurs by cleavage of covalent bonds, two or more new different molecules yield in the active layer. Therefore, we need to know how many kinds of molecules exist in the active layer after driving the device.

To clarify the number of compounds, we carried out a diffusion-ordered NMR spectroscopy (DOSY) experiment^{16–18} for the materials in the active layer of the liquid OLED after driving for 50 s. DOSY experiment, a two-dimensional NMR experiment which correlate isotropic chemical shifts and self-diffusion coefficients, provide a way to separate the spectra of different compounds in a mixture based on the difference of the diffusion coefficients of respective chemical species.

Figure 2 shows a DOSY contour plot (7.15–8.50 ppm) of materials in the active layer of the liquid OLED after driving for 50 s. The resonance lines for TEGCz at 8.08, 7.49, 7.45, and 7.21 ppm, shown by black lines, provide almost the same diffusion coefficient, $D \sim 10^{-9.0} \text{ m}^2\text{s}^{-1}$, confirming these peaks originate from the same compound. It is also found from Fig. 2 that the resonance lines at 8.43, 8.18, 7.86, 7.6, 7.53 and 7.26 ppm, shown by red lines, have approximately the identical diffusion coefficient.

The diffusion coefficient depends mainly on the molecular weights under a certain solvent and a fixed temperature. Therefore, the difference of molecular weights can be estimated from the DOSY experiment. At the beginning, we assume that the molecular weight of the degraded molecule is smaller than TEGCz. However, unexpectedly, Fig. 2 clearly shows that the molecular weight of the degraded molecule is larger than TEGCz, because the diffusion coefficient is smaller than that of TEGCz.

Compared to TEGCz, the number of resonance lines in the aromatic region (7–9 ppm) of the ^1H NMR spectra increase for the degraded molecule. Therefore, we assume that some reaction

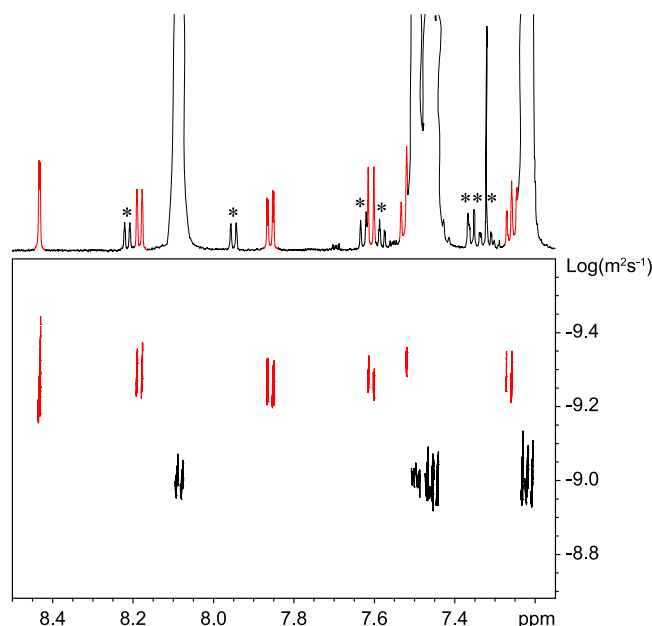


FIG. 2. DOSY contour plot of TEGCz with 0.25 wt% TMP-TFSI after driving for 50 s. For TEGCz, contour lines are plotted between 0.25 % and 59.9 % of the maximum intensity. For the degraded material, contour lines are plotted between 12.9 % and 65.1% of the maximum intensity of the degraded material.

TABLE I. The integrated intensities of M1, D1', D1, and D3' resonance lines.

Driving time	TEGCz	Degradated material, (TEGCz) ₂		
	M1 (8.08 ppm)	D1' (8.43 ppm)	D1 (8.18 ppm)	D3' (7.86 ppm)
0 s	100 %	0 %	0 %	0 %
11 s	100 %	0.34 %	0.35 %	0.34 %
30 s	100 %	0.65 %	0.79 %	0.69 %
50 s	100 %	1.17 %	1.18 %	1.18 %

occurs at the aromatic (carbazole) moiety, during driving the devices. In the carbazole moiety, the nitrogen atom activates the reactivity at the para position (the ortho position is less reactive due to a steric effect).^{19–21} According to the above results and considerations, we reasonably expect that dimerization reactions at para position of carbazole moiety in TEGCz occurs in the devices, which results in the formation of (TEGCz)₂ (Fig. 1(a)).

To confirm the assumption, ¹H NMR experiment was carried out for (TEGCz)₂ with 0.25 wt% TMP-TFSI. To reconcile the experimental conditions, we fabricated the liquid OLEDs with the active layer consisting of (TEGCz)₂ with 0.25 wt% TMP-TFSI and the ¹H NMR experiment was carried out for the materials in the active layer before driving the device. The ¹H NMR spectrum is depicted in Fig. 1(f) along with the assignments (see Fig. S5–S8 of supplementary material).¹⁵ The resonance lines in Fig. 1(f) agree well with newly appeared peaks in the device after driving (Fig. 1(c)–1(e) at 8.43, 8.18, 7.86, 7.6, 7.53 and 7.26 ppm). Only the resonance line at 7.49 ppm observed in Fig. 1(f), which corresponds to the D3 proton of (TEGCz)₂, is not clearly detected in Fig. 1(c)–1(e). However, the resonance lines of D2 and D4 protons of (TEGCz)₂ are doublet and triplet, respectively. The experimental results clearly indicate D2 and D4 are *J*-coupled with one and two adjacent protons, respectively. This is the definite evidence that D3 proton exists in the degraded compound. Thus, we concluded that the resonance line at 7.49 ppm, assigned to D3 in (TEGCz)₂, exists and is simply overlapped with the resonance line of TEGCz in Fig. 1(c)–1(e). Not only for carbazole moiety, all the resonance lines of (TEGCz)₂ including ethylene glycol unit were found in ¹H NMR spectra of the devices after driving (see Fig. S9–S11 of supplementary material).¹⁵ In our experiments, other chemical degradations of TEGCz, such as cleavages of ethylene glycol chains and those of C–N, C–C bonds in carbazole moiety, were not detected within experimental error in operating OLEDs.

The ¹H NMR measurements were carried out with fully-relaxed conditions. Therefore, the molar ratios of the degraded species in the active layer can be analyzed quantitatively from the integrated intensities of the respective resonance lines. Table I shows the integrated intensities of ¹H NMR spectra for the resonance lines at 8.08 (¹H in TEGCz), 8.43, 8.18, 7.86 ppm (¹Hs in the degraded molecule, (TEGCz)₂). The integrated intensities of resonance lines for (TEGCz)₂, D1', D1, and D3', agree with each other within experimental error. The intensities of these resonance lines increase up to ~1% of the TEGCz with increasing the device driving time, 11, 30, and 50 s. The dimerization reactions of TEGCz are found to proceed by driving the devices.

IV. CONCLUSIONS

In this study, we have analyzed the material degradation in the liquid OLEDs consisting of the liquid organic semiconductor, TEGCz, in the active layer. ¹H and DOSY NMR experiments in this study provide quantitative information on the molecular-level degradations; on the reactions of molecules during driving the devices, and on the identification and quantification of degraded materials. From these experiments, we found that the dimerization reaction occurs for the liquid organic semiconductor, TEGCz, in the liquid OLED during driving the devices. This reaction is considered to be related to the device degradation. The results provide not only clarification of degradation mechanisms in liquid OLEDs but also useful design guidelines for materials with long lifetime. From the analysis, the introduction of substituent groups at the para position of carbazole moiety in TEGCz is considered to be one of the effective ways to increase the device lifetime. Such

analysis for device degradations will become increasingly important in organic electronics, not only for liquid but also for solid-state devices. The analysis of degradations for solid-state OLEDs is also now in progress in our laboratory.

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